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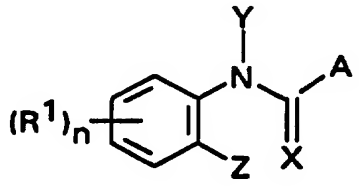

(I)

(57) Abstract

Compounds of formula (I), wherein A is a 5-membered optionally substituted, heteroaryl group comprising at least one hetero atom selected from nitrogen, sulfur and oxygen, which is optionally substituted by one or more of the group R^2; R^1 is alkyl, cycloakyl, cycloalkenyl, alkenyl, alkynyl, or amino (each of which is optionally substituted), Y^1-X-, halogen, cyano, nitro, acyl, acyloxy, optionally substituted heterocyclyl or optionally substituted phenyl; or two adjacent groups together with the carbon atoms to which they are attached can form an optionally substituted benzo ring; R^2 has the same meaning as R^1 or two adjacent groups together with the carbon atoms to which they are attached can form an optionally substituted heterocyclic ring; Y is alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl, each of which is optionally substituted, hydrogen or acyl; Y^1 has the same meaning as Y or is optionally substituted phenyl or optionally substituted heterocyclyl; Z is $C(=X^1)-X^2-R^3$, cyano, nitro, amino, acyl, optionally substituted heterocyclyl, $-C(R^5)=N-OR^6$ or $-C(R^5)=N-NR^6R^7$; R^3 is alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, phenyl or heterocyclyl, each of which is optionally substituted, hydrogen or an inorganic or organic cationic group; X^1 and X^2, which may be the same or different, are O or S; R^5, R^6 and R^7 which may be the same or different, are alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, phenyl or heterocyclyl, each of which is optionally substituted or hydrogen or R^6 and R^7 together with the atom(s) to which they are attached can form a ring; and n is 0 to 4, have fungicidal activity.

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DERIVATIVES OF ANTHRANILIC ACID USEFUL AS FUNGICIDES

Field of the invention

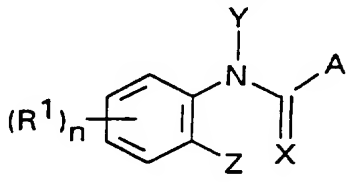
This invention relates to new derivatives of anthranilic acid useful as fungicides.

Prior Art

In GB 1,563,664 and Japanese Kokai 53130655 and 53072825, there are disclosed fungicidal esters of anthranilic acid. We have found that certain novel anthranilic acid derivatives also have valuable fungicidal activity and also have advantages over compounds disclosed in these publications.

Disclosure of the invention

According to the invention there is provided a compound of formula I



(I)

wherein

A is a 5 membered optionally substituted, heteroaryl group comprising at least one hetero atom selected from nitrogen, sulfur and oxygen, which is optionally substituted by one or more of the group R^2;

R^1 is alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, or amino, (each of which is optionally substituted), Y^1-X-, halogen, cyano, nitro, acyl, optionally substituted heterocyclyl or optionally substituted phenyl; or two adjacent groups together with the carbon atoms to which they are attached can form an optionally substituted benzo ring;

R^2 has the same meaning as R^1 or two adjacent groups together with the carbon atoms to which they are attached can form an optionally substituted heterocyclic ring;

Y is alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl, each of which is optionally substituted, hydrogen or acyl;

Y^1 has the same meaning as Y or is optionally substituted phenyl or optionally substituted heterocyclyl;

Z is $C(=X^1)-X^2-R^3$, cyano, nitro, amino, acyl, optionally substituted heterocyclyl, $-C(R^5)=N-OR^6$ or $-C(R^5)=N-NR^6R^7$;

R^3 is alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, phenyl or heterocyclyl, each of which is optionally substituted, hydrogen or an inorganic or organic cationic group;

X^1 and X^2, which may be the same or different, are O or S;

R^5, R^6 and R^7, which may be the same or different, are alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, phenyl or heterocyclyl, each of which is optionally substituted or hydrogen or R^6 and R^7 together with the atom(s) to which they are attached can form a ring; and

n is 0 to 4,

together with complexes with metal salts, as well as salts with bases of compounds which are acids and salts with acids of compounds which are bases, with the proviso that when Z is methoxycarbonyl and Y is hydrogen and ring A is furyl or thienyl, then either n is not 0 or ring A is substituted.

Examples of rings that A can be include, thiophene, furan, pyrrole, pyrazole, imidazole, thiazole, isothiazole, oxazole, isoxazole, thiadiazole, oxadiazole and triazole. When the ring comprises a sulfur atom this may be in an oxidised state either as sulfoxide or sulfone.

In a particularly preferred group of compounds Z is methoxycarbonyl.

Alkyl groups are preferably of 1 to 20, eg 1 to 6, carbon atoms. Alkenyl and alkynyl groups are generally of 3 to 6 carbon atoms. Cycloalkyl or cycloalkenyl groups are preferably of 3 to 8 carbon atoms.

Substituents, when present on any alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, alkoxy or alkylthio group, include halogen, cyano, alkoxy (e.g. of 1 to 4 carbon atoms, and which may be substituted, e.g. by halo), hydroxy, alkylthio, nitro, optionally substituted amino, carboxy, alkoxycarbonyl, acyl, acyloxy, heterocyclyl and aryl.

Cycloalkyl or cycloalkenyl groups may also be substituted by alkyl.

Aryl groups are usually phenyl, optionally substituted, e.g. by one or more of the same groups as defined for R^1.

The term heterocyclyl includes both aromatic and non-aromatic heterocyclyl groups. Heterocyclyl groups are generally 5, 6 or 7-membered rings containing up to 4 hetero atoms selected from nitrogen, oxygen and sulfur. Examples of heterocyclyl groups are furyl, thienyl, pyrrolyl, pyrrolinyl, pyrrolidinyl, imidazolyl, dioxolanyl, oxazolyl, thiazolyl, imidazolidinyl, pyrazolyl, pyrazolinyl, pyrazolidinyl, isoxazolyl, isothiazolyl, oxadiazolyl, triazolyl, thiadiazolyl, pyranyl, pyridyl, piperidinyl, dioxanyl, morpholino, dithianyl, thiomorpholino, pyridazinyl, pyrimidinyl, pyrazinyl, piperazinyl, triazinyl, thiazolinyl, benzimidazolyl, tetrazolyl, benzoxazolyl, imidazopyridinyl, 1,3-benzoxazinyl, 1,3-benzothiazinyl, oxazolopyridinyl, benzofuranyl, quinolinyl, quinazolinyl, quinoxalinyl, sulfolanyl, dihydroquinazolinyl, benzothiazolyl, phthalimido, benzofuranyl, azepinyl, oxazepinyl, thiazepinyl, diazepinyl and benzodiazepinyl. Heterocyclyl groups may themselves be substituted for example as for phenyl.

Amino groups may be substituted for example by one or two optionally substituted alkyl, acyl or sulfonyl groups, or two substituents can form a ring, preferably a 5 to 7-membered ring, which may be substituted and may contain other hetero atoms, for example morpholine, thiomorpholine, or piperidine.

The term acyl includes the residue of sulfur and phosphorus-containing acids as well as carboxylic acids. Examples of acyl groups are thus $-COR^5$, $-COOR^5$, $-CXNR^5R^6$, $-CON(R^5)OR^6$, $-COONR^5R^6$, $-CON(R^5)NR^6R^7$, $-COSR^5$, $-CSSR^5$, $-S(O)_pR^5$, $-S(O)_2OR^5$, $-S(O)_pNR^5R^6$, $-P(=X)(OR^5)(OR^6)$, $-CO-COOR^5$, where R^5, R^6 and R^7 are as defined previously, or R^6 and R^7 together with the atom(s) to which they are attached can form a ring, p is 1 or 2 and X is O or S.

Complexes of compounds of the invention are usually formed from a salt of formula MAn_2, in which M is a divalent metal cation, e.g. copper, manganese, cobalt, nickel, iron or zinc and An is an anion, e.g. chloride, nitrate or sulfate.

The compounds of the invention have activity against a wide range of pathogens of Deuteromycete, Ascomycete, Phycomycete and Basidiomycete origin, and especially against fungal diseases of plants, e.g. mildews and particularly cereal powdery mildew (*Erysiphe graminis*) and vine downy mildew (*Plasmopara viticola*), rice blast (*Pyricularia oryzae*), rice sheath blight (*Pellicularia sasakii*), apple scab (*Venturia inaequalis*), grey mould (*Botrytis cinerea*) and glume blotch (*Leptosphaeria nodorum*).

The compounds of the invention are generally formulated in conventional compositions used for fungicides. These compositions can contain one or more additional pesticides, for example compounds known to possess herbicidal, fungicidal, insecticidal, acaricidal or nematicidal properties.

The diluent or carrier in the composition of the invention can be a solid or a liquid optionally in association with a surface-active agent, for example a dispersing agent, emulsifying agent or wetting agent. Suitable surface-active agents include anionic compounds such as a carboxylate, for example a metal carboxylate of a long chain fatty acid; an N-acylsarcosinate; mono- or di-esters of phosphoric acid with fatty alcohol ethoxylates or salts of such esters; fatty alcohol sulfates such as sodium dodecyl sulfate, sodium octadecyl sulfate or sodium cetyl sulfate; ethoxylated fatty alcohol sulfates; ethoxylated alkylphenol sulfates; lignin sulfonates; petroleum sulfonates; alkyl-aryl sulfonates such as alkyl-benzene sulfonates or lower alkylnaphthalene sulfonates, e.g. butyl-naphthalene sulfonate; salts of sulfonated naphthalene-formaldehyde condensates; salts of sulfonated phenol-formaldehyde condensates; or more complex sulfonates such as the amide sulfonates, e.g. the sulfonated condensation product of oleic acid and N-methyl taurine or the dialkyl sulfosuccinates, e.g. the sodium sulfonate of dioctyl succinate. Nonionic agents include condensation products of fatty acid esters, fatty alcohols, fatty acid amides or fatty-alkyl- or alkenyl-substituted phenols with ethylene oxide, fatty esters of polyhydric alcohol ethers, e.g. sorbitan fatty acid esters, condensation products of such esters with ethylene oxide, e.g. polyoxyethylene sorbitan fatty acid esters, block copolymers of ethylene oxide and propylene oxide, acetylenic glycols such as 2,4,7,9-tetramethyl-

5-decyne-4,7-diol, or ethoxylated acetylenic glycols. Examples of a cationic surface-active agent include, for instance, an aliphatic mono-, di-, or polyamine as an acetate, naphthenate or oleate; an oxygen-containing amine such as an amine oxide or polyoxyethylene alkylamine; an amide-linked amine prepared by the condensation of a carboxylic acid with a di- or polyamine; or a quaternary ammonium salt.

The compositions of the invention can take any form known in the art for the formulation of agrochemicals, for example, a solution, a dispersion, an aqueous emulsion, a dusting powder, a seed dressing, a fumigant, a smoke, a dispersible powder, an emulsifiable concentrate or granules. Moreover it can be in a suitable form for direct application or as a concentrate or primary composition which requires dilution with a suitable
quantity of water or other diluent before application.

As a dispersion, the composition comprises a compound of the invention dispersed in a liquid medium, preferably water. It is often convenient to supply the consumer with a primary composition which can be diluted with water to form a dispersion having the desired concentration. The primary composition can be provided in any one of the following forms. It can be a dispersible solution which comprises a compound of the invention dissolved in a water-miscible solvent with the addition of a dispersing agent. A further alternative comprises a compound of the invention in the form of a finely ground powder in association with a dispersing agent and intimately mixed with water to give a paste or cream which can if desired be added to an emulsion of oil in water to give a dispersion of active ingredient in an aqueous oil emulsion.

An emulsifiable concentrate comprises a compound of the invention dissolved in a water-immiscible solvent together with an emulsifying agent and which is formed into an emulsion on mixing with water.

A dusting powder comprises a compound of the invention intimately mixed with a solid pulverulent diluent, for example, kaolin.

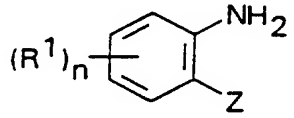
A granular solid comprises a compound of the invention associated with similar diluents to those which may be employed in dusting powders, but the mixture is granulated by known methods. Alternatively it comprises the active ingredient adsorbed or absorbed on a pre-granular diluent, for example, Fuller's earth, attapulgite or limestone grit.

A wettable powder usually comprises the active ingredient in admixture with a suitable surfactant and an inert powder diluent such as china clay.

Another suitable concentrate, particularly when the product is a solid, is a flowable suspension concentrate which is formed by grinding the compound with water, a wetting agent and a suspending agent.

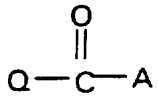
The concentration of the active ingredient in the composition of the present invention is preferably within the range of 1 to 30 per cent by weight, especially 5 to 30 per cent by weight. In a primary composition the amount of active ingredient can vary widely and can be, for example, from 5 to 95 per cent by weight of the composition.

The compounds of the invention may be prepared in known manner, for example by reacting a compound of formula II



(II)

with a compound of formula III



(III)

where Q is a leaving group, preferably a halogen and especially chlorine, to give a compound of formula I, where X is O and Y is hydrogen, and if desired modifying this compound in known manner to give other compounds where X and/or Y have other desired values, and if desired modifying compounds of formula I in known manner to give compounds where R^1 has other values.

The reaction between compounds II and III is generally carried out in the presence of a base, e.g. an organic tertiary amine and preferably in the presence of a solvent, e.g. an ether.

The compounds of formula II and III are either known or can be prepared in known manner.

Where A is a sulfur containing ring, the sulfur can be oxidised in known manner.

The invention is illustrated in the following examples. Structures of isolated novel compounds were confirmed by elemental and/or other appropriate analyses. Temperatures are in °C.

Example 1

A stirred mixture of 5-bromo-2-furancarboxylic acid (5 g) in dry toluene was treated with phosphoryl chloride (2.9 ml) and the mixture stirred at room temperature overnight. Methyl anthranilate (3.93 g) and triethylamine (3.63 ml) were added dropwise with ice-bath cooling and the mixture stirred at room temperature overnight. Ethyl acetate was added and the mixture partitioned with water. The organic layer was washed with aqueous sodium hydrogen carbonate and brine, dried and evaporated. The residue was washed with light petroleum and recrystallised from acetonitrile to give methyl N-(5-bromo-2-furancarbonyl)-anthranilate, m.p. 170-1.5°. (compound 1)

Example 2

A solution of methyl anthranilate (4.3 g) and triethylamine (3.93 ml) in tetrahydrofuran was added dropwise with ice-bath cooling and stirring to a solution of 5-nitro-2-furancarbonyl chloride (5 g) in tetrahydrofuran. The mixture was stirred for 5 hours, and evaporated under reduced pressure. The residue was washed with water, dissolved in dichloromethane and the organic extract washed with aqueous sodium hydrogen carbonate and brine, dried and evaporated. The residue was washed with light petroleum to give methyl N-(5-nitro-2-furan-carbonyl)anthranilate, m.p. 179-81°. (compound 2)

Example 3

Compound 1 from Example 2 (1 g) was treated with methanolic sodium methoxide under reflux. The mixture was cooled, poured into water acidified with acetic acid and extracted with ethyl acetate. The extract was washed in turn with water and brine, dried over magnesium sulfate and evaporated. The residue was purified by silica gel column chromatography to give methyl N-(5-methoxy-2-furan-carbonyl)anthranilate, m.p. 109-10.5°. (compound 3)

Example 4

A stirred mixture of 4-methoxy-5-methoxycarbonyl-2-thiophenecarboxylic acid (1 g) and thionyl chloride (5 ml) was heated under reflux for 9 minutes. The mixture was cooled, evaporated and the residue (comprising crude 4-methoxy-5-ethoxycarbonyl-2-furancarbonyl chloride) was treated with methyl anthranilate and triethylamine in a similar manner to Example 1. The reaction mixture was poured into water and the precipitate collected, washed with water and dried to give methyl N-(4-methoxy-5-methoxycarbonyl-2-thiophenecarbonyl)anthranilate, m.p. 176-9°. (compound 4)

Example 5

A mixture of 2-methoxy-1-methyl-5-imidazolecarboxylic acid (1 g) and 2-chloro-1-methylpyridinium chloride (1.8 g) in acetonitrile was stirred at room temperature for 15 minutes. Triethylamine (1.4 g was added and the mixture stirred at room temperature for 4 hours to give crude 2-[2-methoxy-1-methyl-5-imidazole-carbonyl)-1-methylpyridinium chloride. Methyl anthranilate (0.97 g) was added and the mixture heated under reflux for 18 hours. It was evaporated under reduced pressure and the residue dissolved in dichloromethane and the organic extract washed with water, aqueous sodium hydrogen carbonate, water, dried and evaporated. The residue was washed triturated with light petroleum and the resultant oil treated with ether and filtered. The ether solution was evaporated and the residue purified by silica gel chronmatography to give methyl N-(2-methoxy-1-methyl-5-imidazolecarbonyl)anthranilate, m.p. 112-3°. (compound 5)

Example 6

Sodium hydride (0.16 g of a 60% dispersion in oil) was added with stirring at room temperature to a solution of the compound 13 (see later) (1.04 g) in dry tetrahydrofuran (30 ml). The mixture was stirred for 15 minutes and then methyl iodide (0.5 ml) was added. The mixture was stirred at room temperature for 3 hours, left to stand overnight and poured into brine. It was then extracted with ethyl acetate. The extract was washed in turn with water and brine, dried over magnesium sulfate and evaporated. The residue was purified by silica gel column chromatography to give methyl N-(3-methoxy-5-isoxazolecarbonyl)-N-methylanthranilate, m.p. 61-3°. (compound 6)

Example 7

In a similar manner to one of the previous Examples the following compounds were obtained

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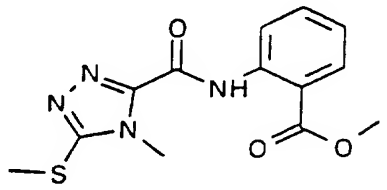
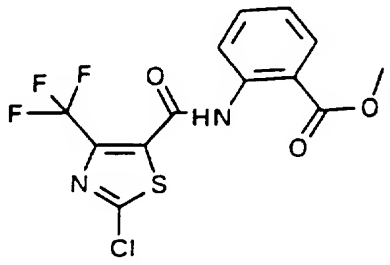
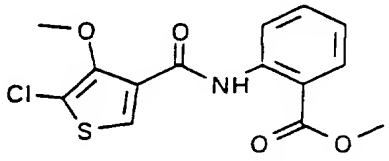
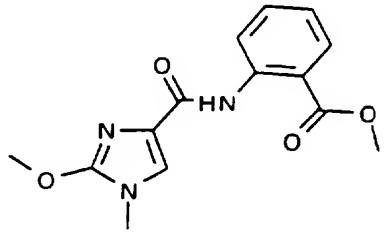
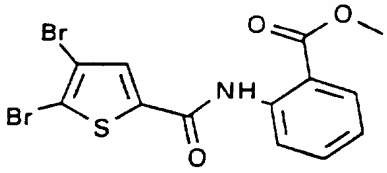
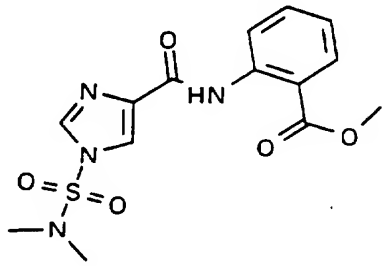
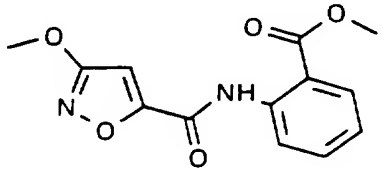
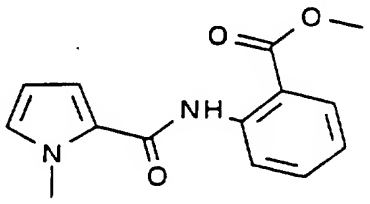
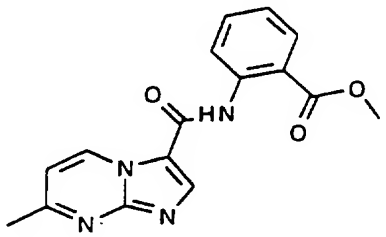
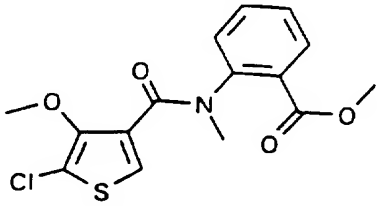
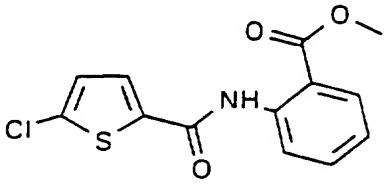
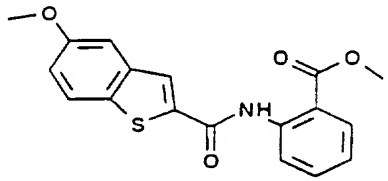
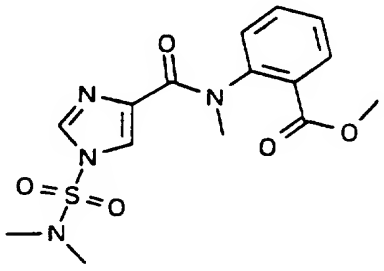
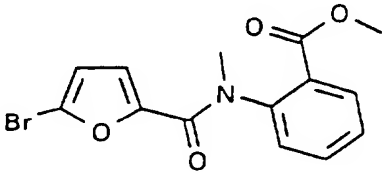
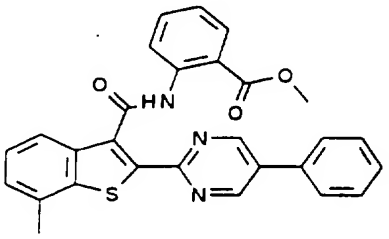
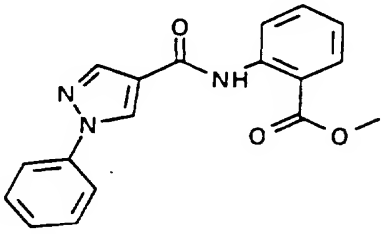
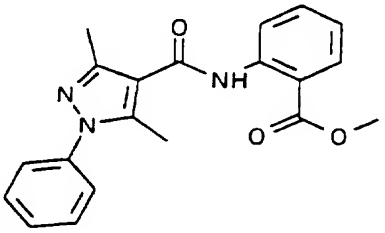
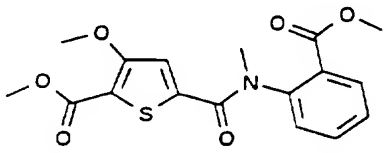
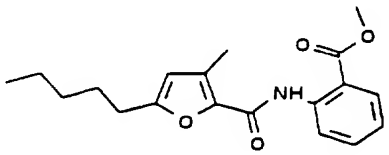
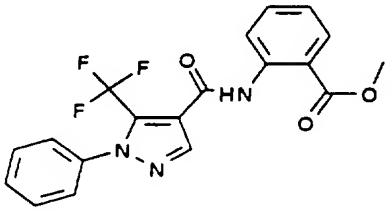
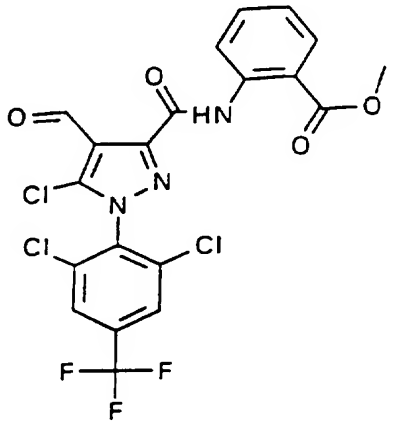
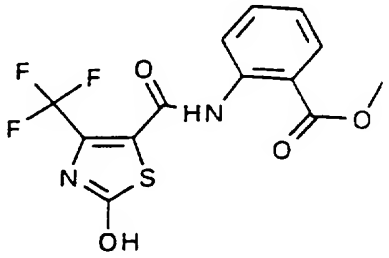
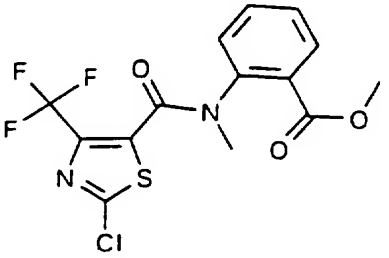
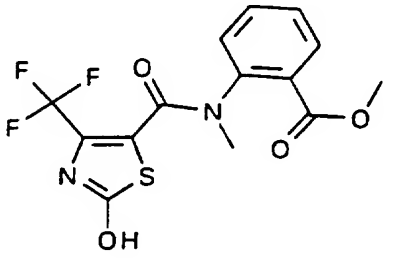
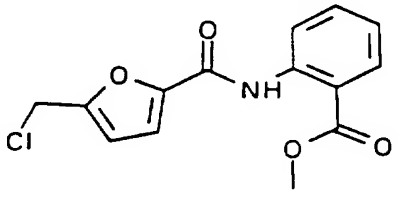
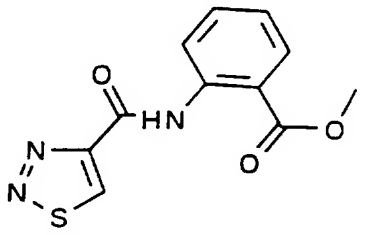
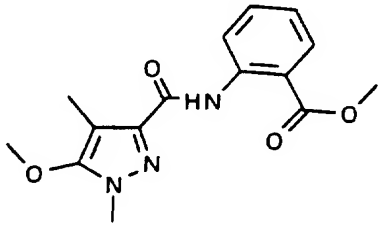
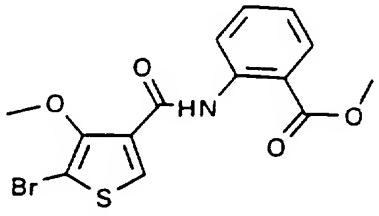
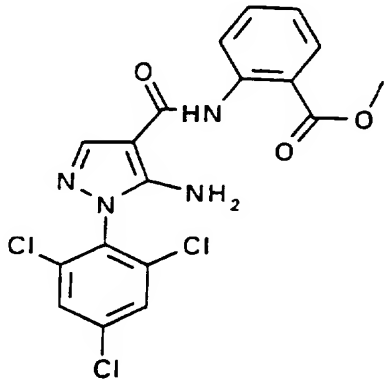
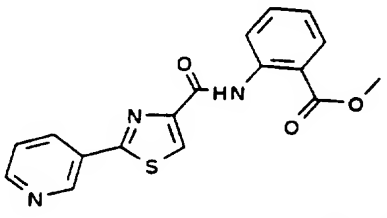
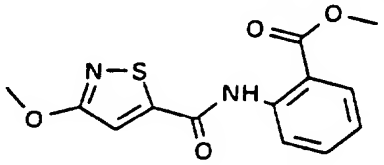
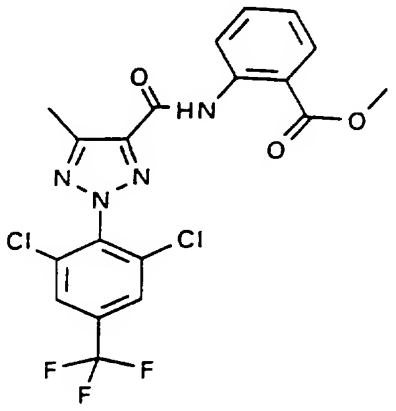
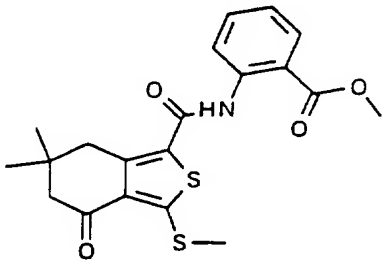
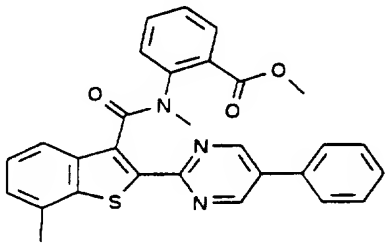
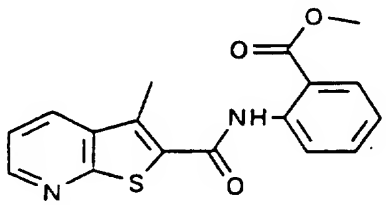
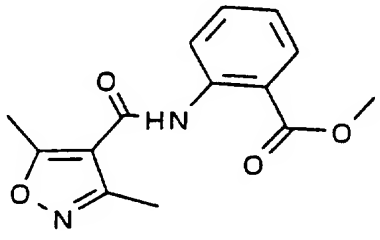
7		198-200
8		121.5-3
9		oil
10		138-9
11		175-7
12		179-81
13		158-9.5

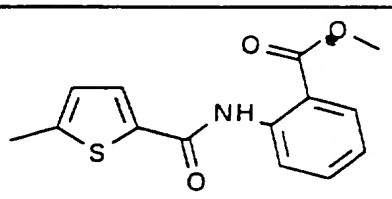
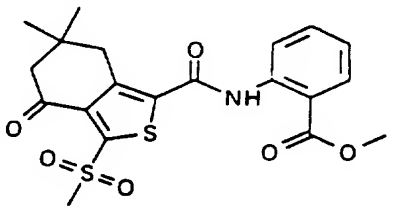
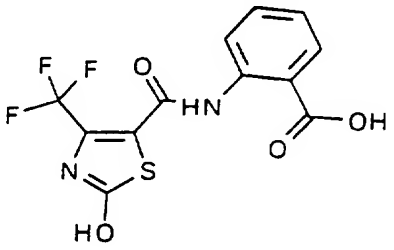
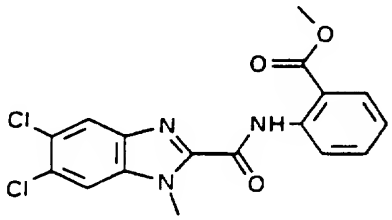
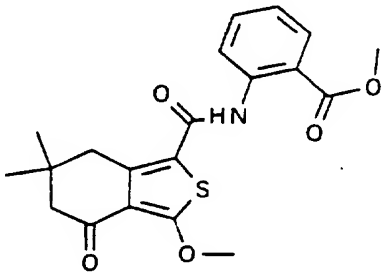
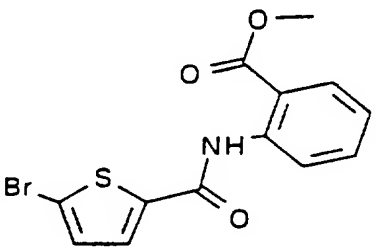
14		149.5-51.5
15		210
16		oil
17		113-15
18		145.5-7.5
19		135-7
20		62-4

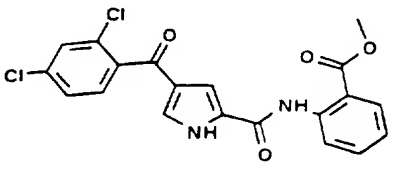
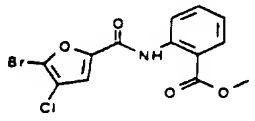
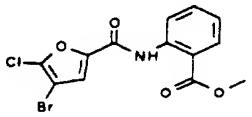
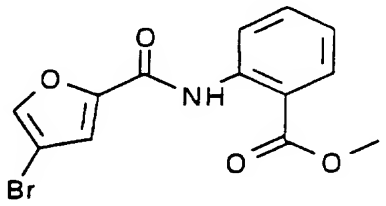
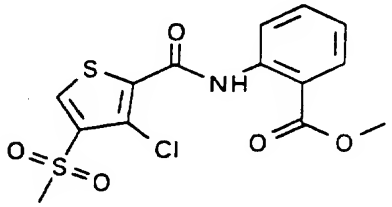
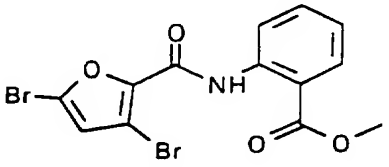
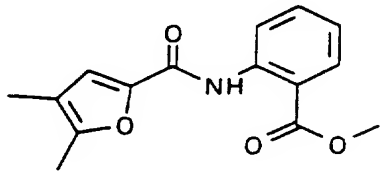
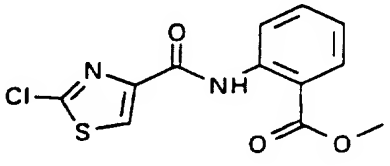
21		215-16
22		150-51
23		123-24
24		108-10
25		oil
26		114-16

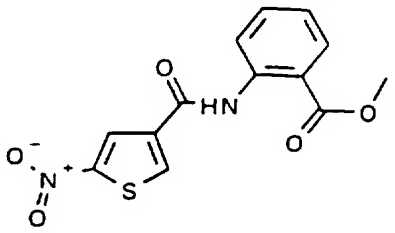
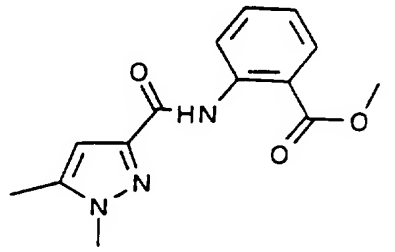
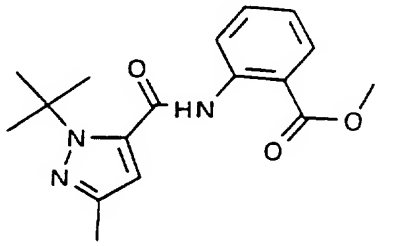
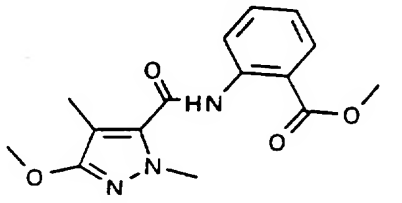
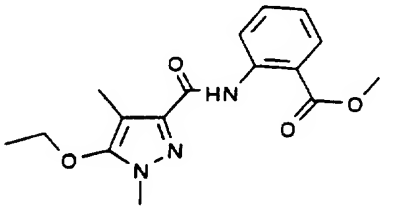
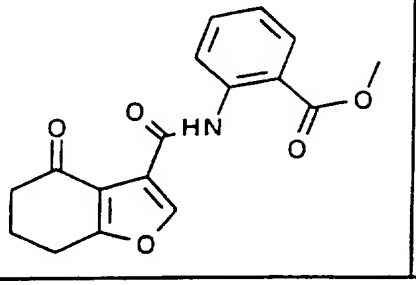
27		196-200
28		215-17
29		95-7.5
30		146-7.5
31		oil

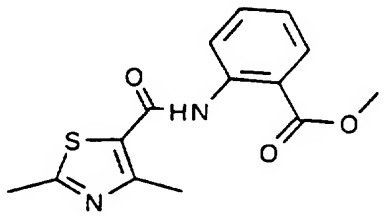
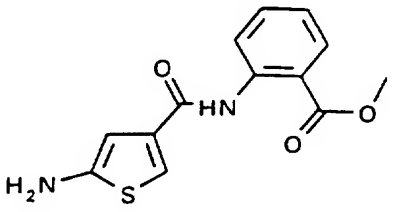
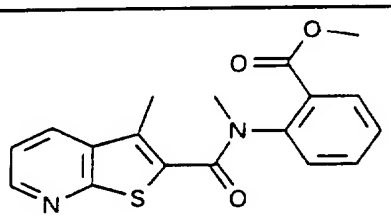
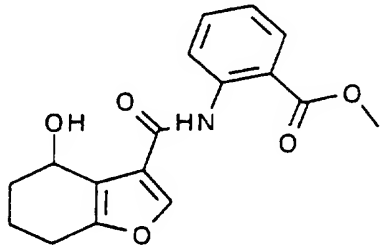
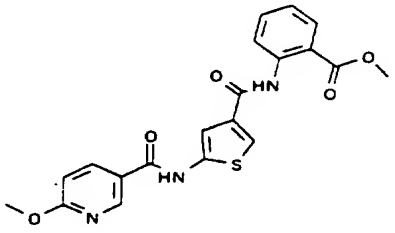
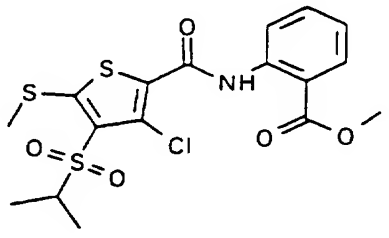
32		185-6
33		138-9
34		112-14
35		219-23
36		186-88
37		161-62.5

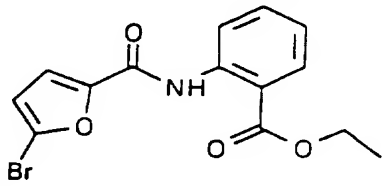
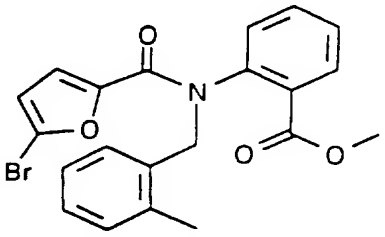
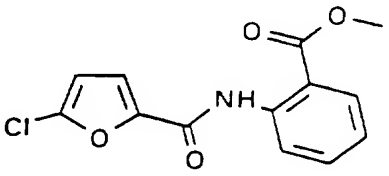
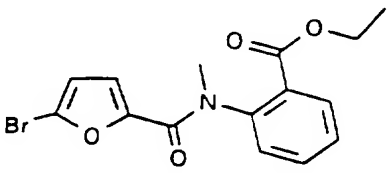
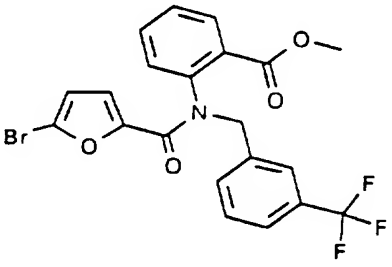
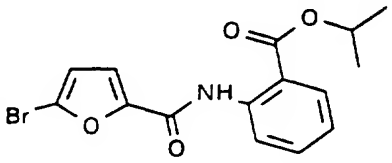
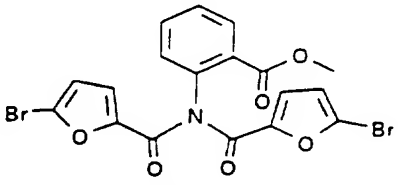
38		171-3
39		184-6
40		232-4
41		184-5
42		117-19

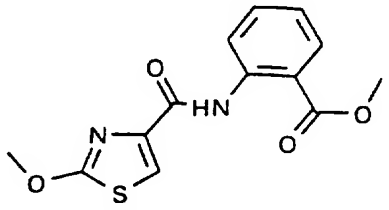
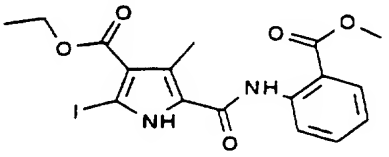
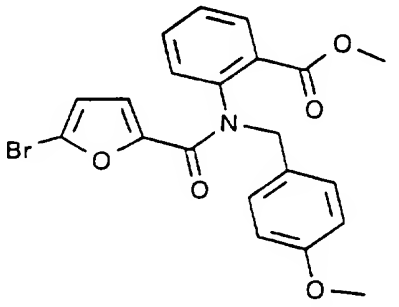
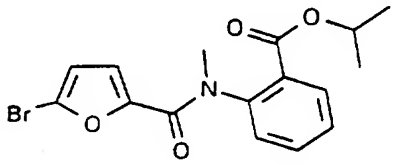
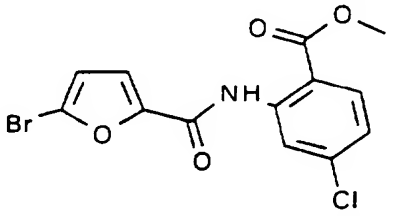
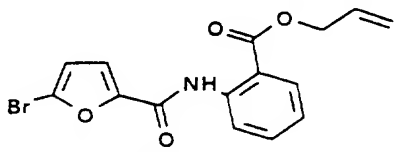
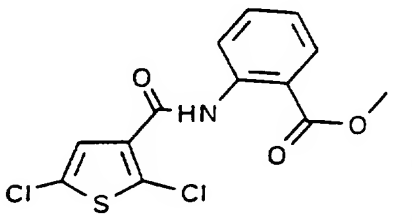
43		91-3
44		211-12
45		189-92
46		189-92
47		190-92
48		114-17

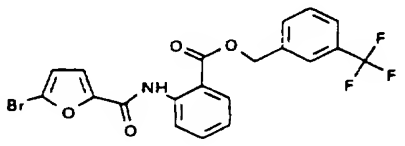
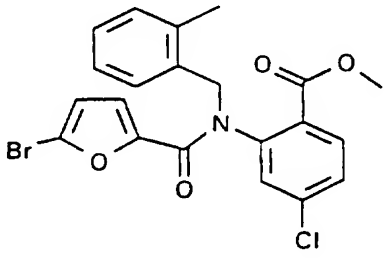
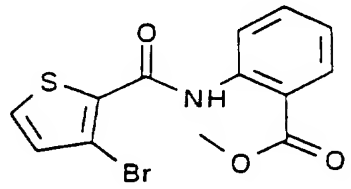
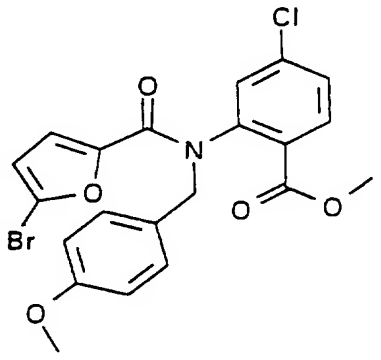
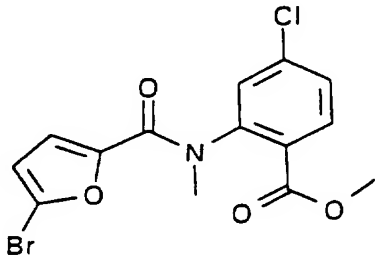
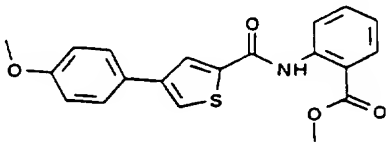
49		184-87
50	 	oil
51		117-20
52		162-64
53		151-2
54		106-7
55		128-30

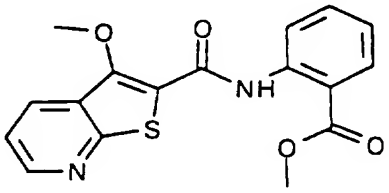
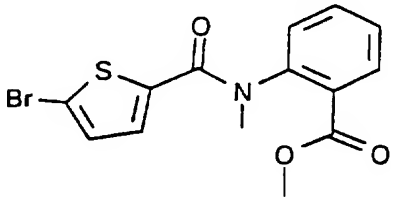
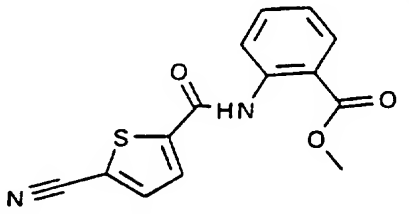
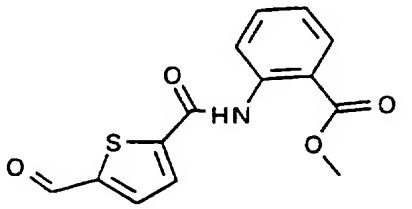
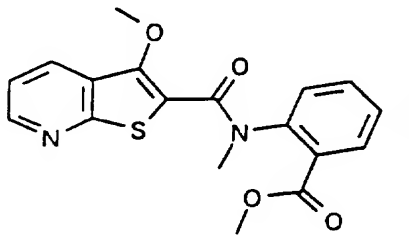
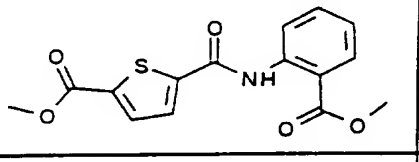
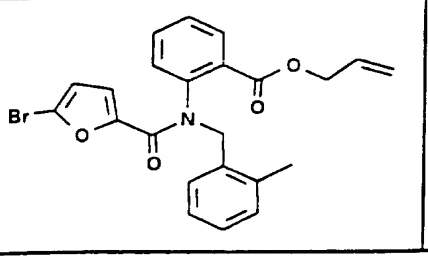
56		154-7
57		97-9
58		103-5
59		132-3
60		108-10
61		155-7

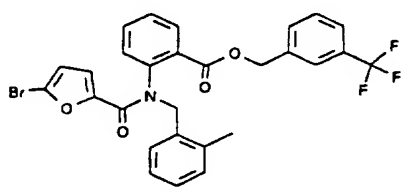
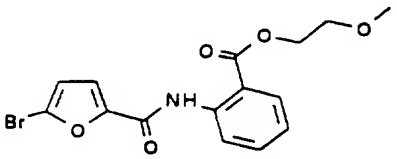
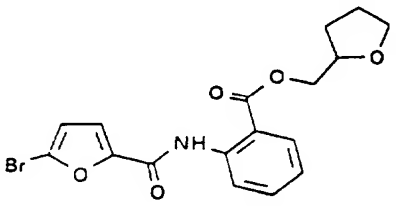
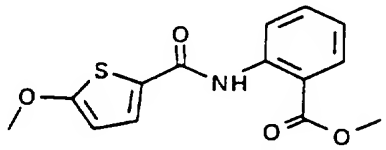
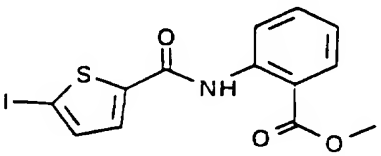
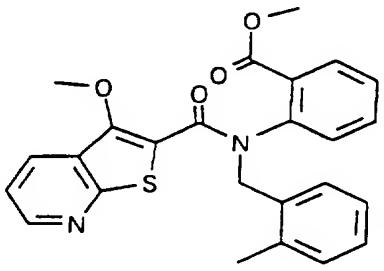
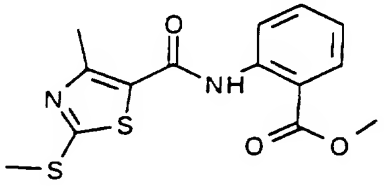
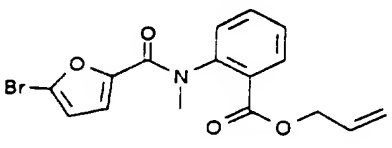
62		150-2
63		121-4
64		111.5-14
65		136-7
66		173-6
67		158-62

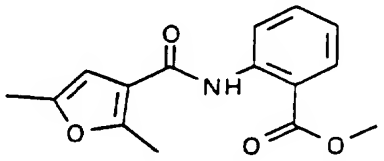
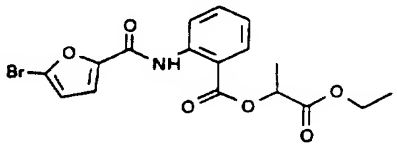
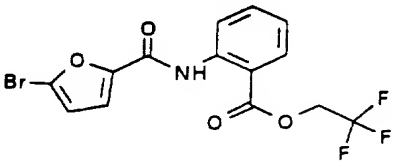
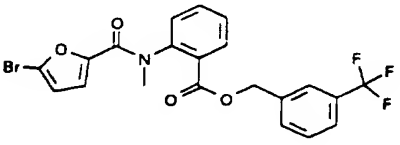
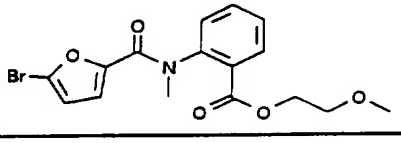
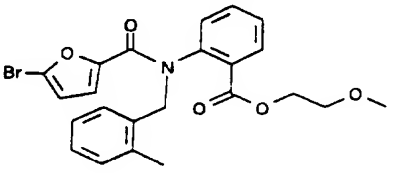
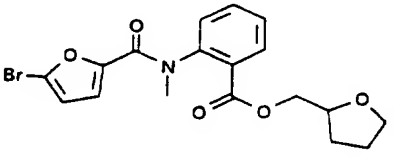
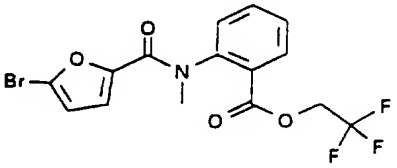
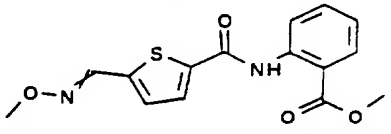
68		98-100
69		118-20
70		122-5
71		oil
72		oil
73		99-101
74		119-20

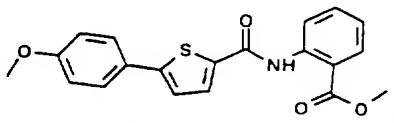
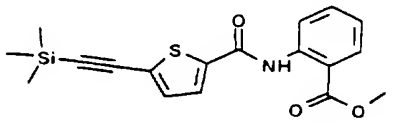
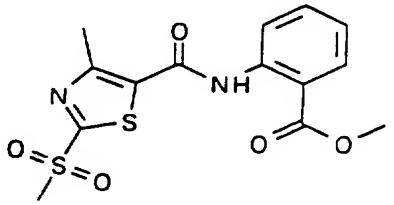
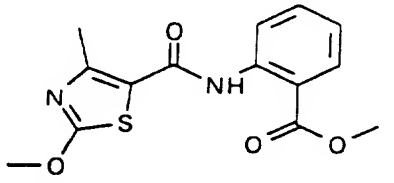
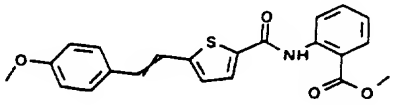
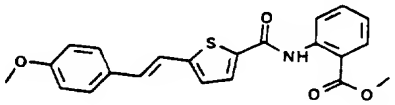
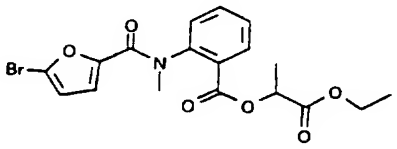
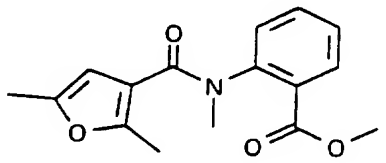
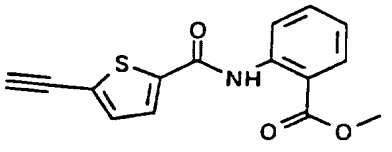
75		230-2
76		163-5
77		112-13
78		76-8
79		134-5
80		119-20
81		125-7

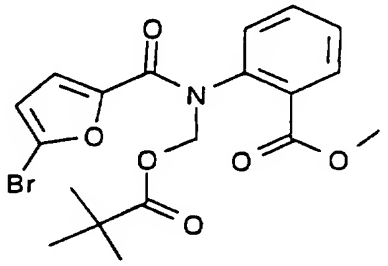
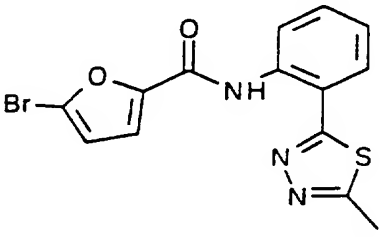
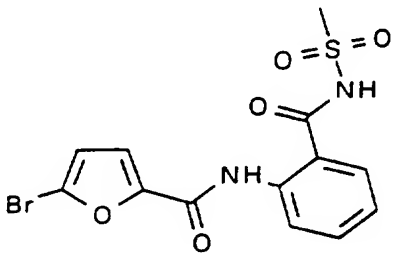
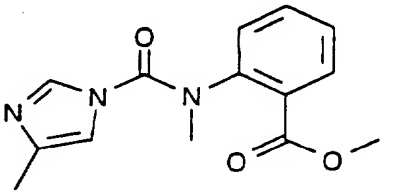
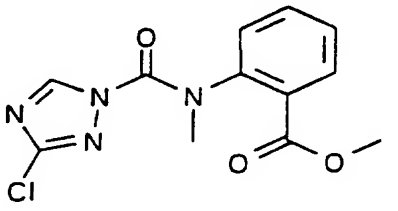
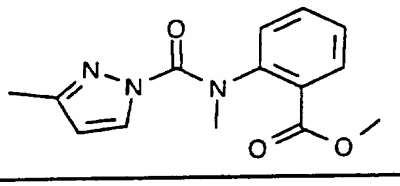
82		130-31
83		107-8
84		153-5
85		104-5
86		114-15
87		139-43

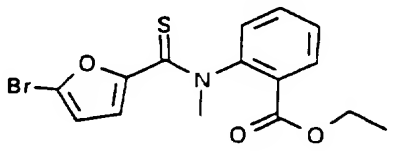
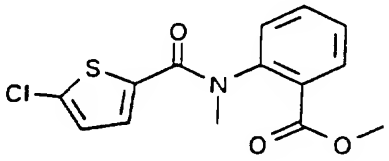
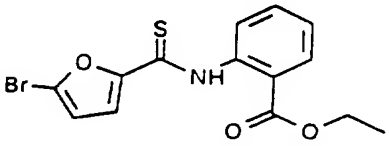
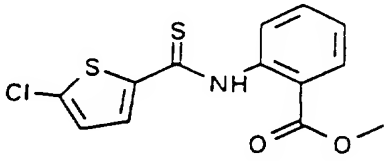
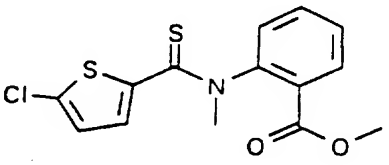
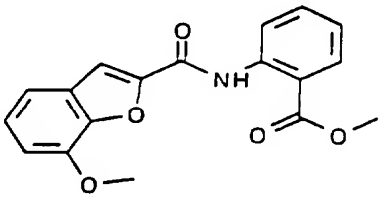
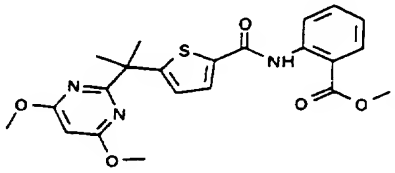
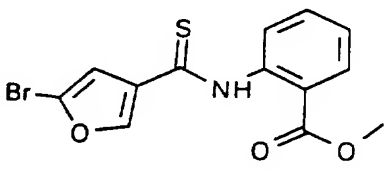
88		178-9
89		oil
90		179-83
91		154-7
92		111-13.5
93		155-57
94		79-80

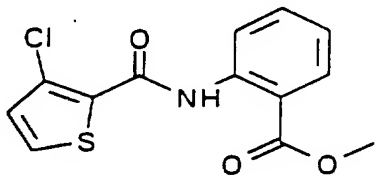
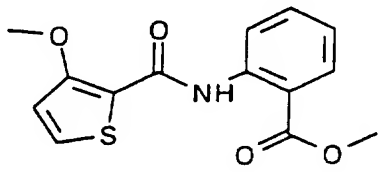
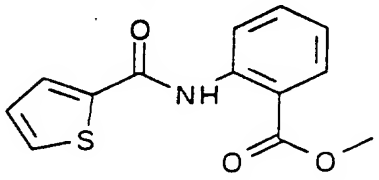
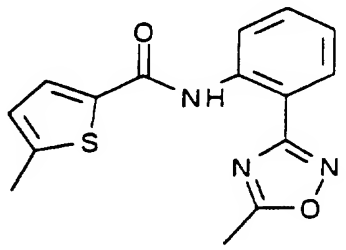
95		89-90
96		103-4
97		96-7
98		130-2
99		138-40
100		oil
101		138.4
102		oil

103		122-3
104		oil
105		171-2
106		
107		75-6
108		82-3
109		116-17
110		89-90
111		125-34

112		144-7
113		159-61
114		169-72
115		brown solid
116		94-129
117		151-2
118		65-6
119		86-7
120		oil

121		oil
122		127-9
123		216-20
124		oil
125		oil
126		oil

127		oil
128		oil
129		98-9
130		172-3
131		121-2
132		141-3
133		106.5-7
134		99-100

135		138-40
136		101-2
137		121-4
138		121-3

Example 8

A mixture of compound 48 (1 g) dichloromethane (20 ml), trifluoroacetic acid (10 ml) and hydrogen peroxide (2 ml; 30%) was stirred at room temperature for two days. The mixture was partitioned between water and dichloromethane and the water phase extracted with dichloromethane. The dichloromethane extracts were washed with aqueous sodium sulphite and brine, dried, filtered and evaporated under reduced pressure. The residue was recrystallised from ethyl acetate to give methyl N-(5-bromo-2-thienylcarbonyl)anthranilate S,S-dioxide, m.p. 142-4°. (Compound 8a)

In a similar manner the following were obtained:

(i) methyl N-(5-chloro-2-thienylcarbonyl)anthranilate S,S-dioxide, m.p. 46-8°. (Compound 8b)

(ii) methyl N-(4,5-dibromo-2-thienylcarbonyl)anthranilate S,S-dioxide, m.p. 165-6°. (Compound 8c)

(iii) methyl N-(2,5-dichloro-3-thienylcarbonyl)anthranilate S,S-dioxide, m.p. 140-2°. (Compound 8d)

(iv) methyl N-(5-methoxybenzo[b]thiophen-2-ylcarbonyl)anthranilate S,S-dioxide, m.p. 127-9°. (Compound 8e)

Test Example

Compounds are assessed for activity against one or more of the following:

Phytophthora infestans: late tomato blight

Plasmopara viticola: vine downy mildew

Erysiphe graminis: barley powdery mildew

Pyricularia oryzae: rice blast

Pellicularia sasakii: rice sheath blight (PS)

Botrytis cinerea: grey mould

Venturia inaequalis: apple scab

Leptosphaeria nodorum: glume blotch

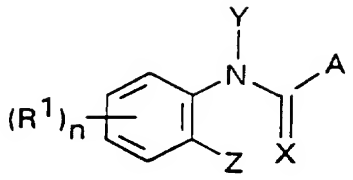
Aqueous solutions or dispersions of the compounds at the desired concentration, including a wetting agent, were applied by spray or by drenching the stem base of the test plants, as appropriate. Plants or plant parts were then inoculated with appropriate test pathogens and kept under controlled environment conditions

suitable for maintaining plant growth and development of the disease. After an appropriate time, the degree of infection of the affected part of the plant was visually estimated. Compounds were considered active if they gave greater than 50% control of the disease at a concentration of 500 ppm (w/v) or less.

Compounds 43, 45, 94 and 100 showed activity against *Phytophthora infestans*; Compounds 2, 4, 9, 10, 12, 18, 20, 28, 29, 30, 32-38, 40, 42, 44, 46, 49, 54, 55, 61, 65, 66, 70, 73, 79, 81, 83-8, 90, 91-7, 100, 103-6, 110-3, 115-20, 123 and 125-7, showed activity against *Plasmopara viticola*;
Compounds 3, 17, 20, 41, 43, 48, 50, 51, 53, 56, 57, 68, 70, 71, 74, 80, 81, 89, 94, 96, 98, 99, 102, 120, 121, 122 and 127 showed activity against *Erysiphe graminis*;
Compounds 6, 16, 22, 23, 31, 64, 69, 72, 81 and 84 showed activity against *Pyricularia oryzae*
Compounds 58 and 74 showed activity *Botrytis cinerea;*
Compounds 3, 8, 9, 15, 33, 46, 56, 58, 70, 78, 80, 82, 89, 94, 107, 108, 109, 114, 118, 119 and126 showed activity against *Venturia inaequalis*, and
Compounds 16, 33, 113 showed activity against *Leptosphaeria nodorum*.

CLAIMS

1. A compound of formula I



(I)

A is a 5 membered optionally substituted, heteroaryl group comprising at least one hetero atom selected from nitrogen, sulfur and oxygen, which is optionally substituted by one or more of the group R^2;

R^1 is alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, or amino, (each of which is optionally substituted), Y^1-X-, halogen, cyano, nitro, acyl, acyloxy, optionally substituted heterocyclyl or optionally substituted phenyl; or two adjacent groups together with the carbon atoms to which they are attached can form an optionally substituted benzo ring;

R^2 has the same meaning as R^1 or two adjacent groups together with the carbon atoms to which they are attached can form an optionally substituted heterocyclic ring;

Y is alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl, each of which is optionally substituted, hydrogen or acyl;

Y^1 has the same meaning as Y or is optionally substituted phenyl or optionally substituted heterocyclyl;

Z is $C(=X^1)$-X^2-R^3, cyano, nitro, amino, acyl, optionally substituted heterocyclyl, $-C(R^5)=N-OR^6$ or $-C(R^5)=N-NR^6R^7$;

R^3 is alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, phenyl or heterocyclyl, each of which is optionally substituted, hydrogen or an inorganic or organic cationic group;

X^1 and X^2, which may be the same or different, are O or S;

R^5, R^6 and R^7, which may be the same or different, are alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, phenyl or heterocyclyl, each of which is optionally substituted or hydrogen or R^6 and R^7 together with the atom(s) to which they are attached can form a ring; and

n is 0 to 4,

together with complexes with metal salts, as well as salts with bases of compounds which are acids and salts with acids of compounds which are bases, with the proviso that when Z is methoxycarbonyl and Y is hydrogen and ring A is furyl or thienyl, then either n is not 0 or ring A is substituted.

2. Fungicidal compositions which comprise a compound as claimed in claim 1 in admixture with an agriculturally acceptable diluent or carrier.

3. A method of combating phytopathogenic fungi at a locus infested or liable to be infested therewith, which comprises applying to the locus a compound as claimed in claim 1.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/EP 95/04800

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07D307/68 A01N43/00 C07D307/73 C07D333/38 C07D233/66
C07D261/18 C07D249/10 C07D277/32 C07D277/34 C07D277/36
C07D207/40 C07D333/70 C07D231/14 C07D231/22 C07D285/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 122, no. 13, 27 March 1995 Columbus, Ohio, US; abstract no. 160414, LEE A R ET AL 'Facile synthesis of N-substituted 2-indolecarboxamides' see abstract & CHIN. PHARM. J. (TAIPEI) (CPHJEP);94; VOL.46 (4); PP.307-11, SCHOOL PHARMACY;NATIONAL DEFENSE MEDICAL CENTER; TAIPEI; TAIWAN (TW), --- -/--	1

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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Date of the actual completion of the international search	Date of mailing of the international search report
29 March 1996	17. 04. 96
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Paisdor, B

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INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/EP 95/04800

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 122, no. 7, 13 February 1995 Columbus, Ohio, US; abstract no. 080950, LIM J K ET AL 'Synthesis of melandrin derivatives' see abstract & YAKHAK HOECHI (YAHOA3,05134234);94; VOL.38 (3); PP.281-5, SUNG KYUN KWAN UNIVERSITY;COLLEGE OF PHARMACY; SUWON; 440-746; S. KOREA (KR), ---	1
X	CHEMICAL ABSTRACTS, vol. 121, no. 23, 5 December 1994 Columbus, Ohio, US; abstract no. 271343, LIM J K ET AL 'Analgesic, anti-inflammatory and antiviral effects of melandrin derivatives' see abstract & YAKHAK HOECHI (YAHOA3,05134234);94; VOL.38 (3); PP.345-50, SUNG KYUN KWAN UNIV.;COLL. PHARM.; SUWON; 440-746; S. KOREA (KR), ---	1
X	CHEMICAL ABSTRACTS, vol. 121, no. 21, 21 November 1994 Columbus, Ohio, US; abstract no. 255694, RAJENDRAN S P ET AL 'Synthesis and utilization of 3-(2'-hydroxyethyl)quinolin-2(1H)-ones. Part-II' see abstract & J. INDIAN CHEM. SOC. (JICSAH,00194522);93; VOL.70 (10); PP.815-18, BHARATHIAR UNIV.;DEPT. CHEM.; COIMBATORE; 641 046; INDIA (IN), ---	1
X	CHEMICAL ABSTRACTS, vol. 115, no. 23, 9 December 1991 Columbus, Ohio, US; abstract no. 256589, BELOKON Y N ET AL 'A novel application of the chiral reagent (S)-N-(N'-benzylprolyl)am inobenzaldehyde - synthesis of.alpha.-methylvaline and.alpha.-methylglutamic acid in optically pure form' see abstract & IZV. AKAD. NAUK SSSR, SER. KHIM. (IASKA6,00023353);91; (7); PP.1536-42, INST. ELEMENTOORG. SOEDIN. IM. NESMEYANOVA;MOSCOW; USSR (SU), --- -/--	1

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INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/EP 95/04800

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,92 17479 (IMPERIAL CHEMICAL INDUSTRIES PLC;UK) 15 October 1992 see CAS-RN [145550-75-0] ---	1
X	JOURNAL OF HETEROCYCLIC CHEMISTRY, vol. 24, no. 1, 1987 PROVO US, pages 223-225, PEET N P 'Reactions of 2-isocyanatobenzoyl chloride and 2-carbomethoxyphenyl isocyanate with 5-aminotetrazole' see page 224; example 6 ---	1
X	SYNTHESIS, no. 1, 1984 STUTTGART DE, pages 68-71, LOONEY-DEAN V ET AL 'Synthesis of derivatives of pyrrole using methyl 2-isothiocyanatobenzoate' see page 69; examples ---	1
X	CHEMICAL ABSTRACTS, vol. 087, no. 17, 24 October 1977 Columbus, Ohio, US; abstract no. 135197, ARYA V P ET AL 'Antihypertensive agents: Part IV. Synthesis and hypotensive activity of certain 2-substituted 4,5-dihydroimidazoles' see abstract & INDIAN J. CHEM., SECT. B (IJSBDB);77; VOL.15B (2); PP.148-53, CIBA-GEIGY RES. CENT.;BOMBAY; INDIA, ---	1
X	TETRAHEDRON, (INCL TETRAHEDRON REPORTS), vol. 33, no. 1, 1977 OXFORD GB, pages 155-157, SIEMION I Z ET AL 'The amide-aromatic-ring system. An inherently dissymmetric chromophore' see page 155, column 1, last paragraph - column 2 --- -/--	1

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INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/EP 95/04800

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 119, no. 19, 8 November 1993 Columbus, Ohio, US; abstract no. 195098u, YONG WHAN KIM ET AL. 'Quantitative structure-activity relationship of N-substituted phenyl-5-chloro-1,3-dimethylpyrazol-4-carb oxamides' page 21; column 1; see abstract & HAN'GUK NONGHWA HAKHOECHI, vol. 35, no. 3, 1992 pages 382-388, ---	1-3
X	CHEMICAL ABSTRACTS, vol. 121, no. 19, 7 November 1994 Columbus, Ohio, US; abstract no. 230435s, JUNG SUL MOON ET AL. 'Synthesis of N-substituted 5-hydroxyanthranilic acid.' page 1058; column 1; see abstract & YAKHAK HOECHI, vol. 37, no. 3, 1993 pages 243-246, ---	1-3
X	PESTICIDE SCIENCE, vol. 38, no. 1, 1993 BARKING GB, pages 1-7, XP 000394080 W. GARY PHILLIPS ET AL. 'Thiazole Carboxanilide Fungicides: ...' see the whole document ---	1-3
X	EP,A,0 279 239 (CIBA GEIGY AG) 24 August 1988 see claims; examples 3.084, 3.097; table 3 ---	1-3
X	US,A,3 725 427 (HARRISON W ET AL) 3 April 1973 see claims; examples ---	1-3
X	DE,A,20 06 471 (UNIROYAL INC.) 27 August 1970 see claims; examples -----	1-3

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INTERNATIONAL SEARCH REPORT

Ir. national application No.
PCT/EP 95/04800

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.: 1 - 3 (searched incompletely)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

Reason: The claims encompass such an enormous amount of compounds that carrying out a complete search is impossible on economic grounds, because the broadness of the claims is such that even by means of on-line searching techniques a complete search was not possible. For this reason the search has been restricted to the embodiments of the claims sufficiently supported by the description, i.e. the search was restricted to the meanings of the group Z for which an example could be found in the description. Even this restricted search revealed so many known compounds falling under the scope of claim 1 that drafting a complete search report was found to be impossible on economic grounds also. Thus the search report is limited to compounds either to compounds with Z being methoxycarbonyl or to compounds having fungicidal activity

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searches without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter nal Application No
PCT/EP 95/04800

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9217479	15-10-92	AU-B-	1435892	02-11-92
		CA-A-	2107675	09-10-92
		EP-A-	0584085	02-03-94
		JP-T-	7502256	09-03-95
EP-A-0279239	24-08-88	AU-B-	610553	23-05-91
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		DE-A-	3875750	17-12-92
		ES-T-	2052612	16-07-94
		JP-A-	63201178	19-08-88
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		SE-B-	395590	22-08-77